

Article

Exploring RF Magnetron Sputtering Growth Composite Thin Film BiFeO₃-Bi₂Fe₄O₉ on C-Plane Al₂O₃ Substrate

Suleiman Kallaev ¹, Sadyk Sadykov ^{1,2}, Anatoly Pavlenko ³, Mansur Ataev ¹, Jiří Majzner ^{4,*}, Farid Orudzhev ¹ , Kamal Giraev ² and Nariman Alikhanov ^{1,2,*} 

¹ Amirkhanov Institute of Physics, Dagestan Federal Research Center, Russian Academy of Sciences, St. M. Yaragskogo 94, 367003 Makhachkala, Russia

² Physical Department, Dagestan State University, St. M. Gadjeva 43-a, 367015 Makhachkala, Russia

³ Federal Research Centre “The Southern Scientific Centre”, Russian Academy of Sciences, 344006 Rostov-on-Don, Russia

⁴ Department of Physics, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technická 2848/8, 61600 Brno, Czech Republic

* Correspondence: majzner@vut.cz (J.M.); alihanov.nariman@mail.ru (N.A.)

Abstract: Nanocomposite films of BiFeO₃-Bi₂Fe₄O₉ were fabricated on a sapphire substrate Al₂O₃ using the method of gas discharge high-frequency cathodic sputtering of a ceramic target with a stoichiometric composition in an oxygen atmosphere. The results of the film analysis using X-ray structural analysis, Raman scattering, XPS, and atomic force microscopy are presented. The lattice parameters, surface topography, chemical composition of the films, concentration, and average sizes of the crystallites for each phase were determined. It was shown that the ratio of the BiFeO₃ to Bi₂Fe₄O₉ phases in the obtained film is approximately 1:2. The sizes of the crystallites range from 15 to 17 nm. The optical and magnetic properties of the nanocomposite layers were studied, and the band gap width and magnetization hysteresis characteristic of ferromagnetic behavior were observed. The band gap width was found to be 1.9 eV for the indirect and 2.6 eV for the direct interband transitions. The magnetic properties are characterized by a hysteresis loop resembling a “wasp-waist” shape, indicating the presence of magnetic anisotropy.

Keywords: multiferroics; BiFeO₃; Bi₂Fe₄O₉; nanocomposite; film



Citation: Kallaev, S.; Sadykov, S.; Pavlenko, A.; Ataev, M.; Majzner, J.; Orudzhev, F.; Giraev, K.; Alikhanov, N. Exploring RF Magnetron Sputtering Growth Composite Thin Film BiFeO₃-Bi₂Fe₄O₉ on C-Plane Al₂O₃ Substrate. *Materials* **2023**, *16*, 6987. <https://doi.org/10.3390/ma16216987>

Academic Editor: Rainer Hippler

Received: 24 September 2023

Revised: 28 October 2023

Accepted: 30 October 2023

Published: 31 October 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The increased interest of researchers in multiferroics, in which ferromagnetic and ferroelectric ordering coexist, is associated with the potential applications [1–3]. The connection between the ferroelectric and ferromagnetic or antiferromagnetic properties in magnetoelectric materials is widely used in multifunctional memory devices and spintronics [3,4]. One of the promising multiferroics is bismuth ferrite BiFeO₃ (and its derivatives), which exhibits high temperatures of ferroelectric ($T_C \approx 1100$ K) and magnetic ordering ($T_N \approx 645$ K) [5]. At room temperature, the crystal structure has the $R3c$ space group. The spontaneous polarization is oriented along the [111] direction of the pseudocubic perovskite unit cell, and the antiferromagnetic ordering of the G-type occurs such that the magnetic moments of the iron ions rotate in a spiral [101]. According to neutron diffraction data, the period of the cycloid is 62 nm [6]. Below the Neel temperature T_N , bismuth ferrite has a complex, spatially modulated, magnetic structure of the cycloidal type, which does not allow for ferromagnetic properties. The destruction of its spatially modulated spin structure is a necessary condition for the occurrence of the magnetoelectric effect, which can be achieved by doping bismuth ferrite with rare-earth elements, creating nanostructured and thin film systems, or under the influence of high magnetic fields and pressures. Another way to suppress modulation is to create multiphase compounds. Recently, a new direction has emerged in condensed matter physics, studying multiphase systems consisting of compounds with different crystallographic structures and types of magnetic ordering, such

as the composite $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$. The questions about the peculiarities of the formation of $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$ composites, the nature of the interaction, and the details of the mechanism linking their magnetic subsystems are currently widely discussed in the scientific literature. In [7–9], it is reported that nanocomposites based on the perovskite-like bismuth orthoferrite BiFeO_3 and the mullite-like ferrite $\text{Bi}_2\text{Fe}_4\text{O}_9$ demonstrate effects related to the exchange interaction at the interface of these phases.

Mullite $\text{Bi}_2\text{Fe}_4\text{O}_9$, which is often observed as an impurity phase of BiFeO_3 in the solid state, also belongs to the family of multiferroics [10,11]. Unlike BiFeO_3 , it has an orthorhombic crystal structure (space group $Pbam$) [12]. The magnetic properties of polycrystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ depend on the synthesis method and the size of the crystallites. A sample with a crystallite size of 200–450 nm, synthesized using ethylenediaminetetraacetic acid [13], exhibits weak magnetization at room temperature. Polycrystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ with a micron-sized grain, obtained by melting, undergoes an antiferromagnetic phase transition at 250–260 K [14,15]. Polycrystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramics with a grain size less than 200 nm are characterized by magnetic hysteresis at room temperature, which disappears upon heating [16].

In recent years, interest in bismuth ferrite has increased due to the discovery of a large magnetoelectric effect (ME) in BiFeO_3 -based films [17]. The observed ME is associated with the destruction of the spatially modulated structure in thin films, which is caused by high internal strain fields (due to the lattice mismatch between the film and substrate) [18]. Therefore, the development of technology for obtaining thin structures of multiferroic materials based on BiFeO_3 on different substrates becomes a relevant direction.

It should also be noted that $\text{BiFeO}_3/\text{Bi}_2\text{Fe}_4\text{O}_9$ nanocomposites exhibit higher photocatalytic activity (compared to pure BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ individually) in the decomposition of rhodamine B and in the production of H_2 from water under visible light. Such a heterostructure of $\text{BiFeO}_3/\text{Bi}_2\text{Fe}_4\text{O}_9$ and its synthesis strategy can provide new insights into the development of highly efficient photocatalysts [19].

This work presents the results of the synthesis and investigations of the structure, morphology, and optical and magnetic properties of a nanocomposite film $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$, synthesized on an Al_2O_3 sapphire substrate. To the best of our knowledge, there are few studies on thin films of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$.

2. Materials and Methods

Gas discharge RF sputtering of BiFeO_3 films was carried out on a “Plasma 50SE” installation (Manufacturer: ELITEH LLC, Moscow, Russia), designed for producing thin single-crystal films of complex oxides by reactive RF sputtering. The diagram of experimental setup for producing heteroepitaxial films is shown in Figure 1. Single-crystal Al_2O_3 (c-plane) 0.5 mm thick was used as a substrate. The initial temperature of the substrate is ~673 K, the oxygen pressure in the chamber is 80 Pa, the input RF power is 140 W. A ceramic disk of stoichiometric composition BiFeO_3 with a diameter of 50 mm and a thickness of 3 mm was used as a sputtering target.

An X-ray diffraction pattern of a thin film sample on a substrate was taken on an XRD-7000 diffractometer from Shimadzu (Kyoto, Japan). The sample was placed on an attachment for studying thin films and shooting was carried out. The shooting parameters were as follows: tube voltage 30 kV; current 30 mA; X-ray wavelength $\lambda_{\text{CuK}\alpha} = 0.15406$ nm; ray focusing scheme—grazing reflection geometry (grazing incidence X-Ray diffraction—GIXD); incident beam slit $DS = 0.15^\circ$; graphite monochromator on a reflected beam; the angle of the incident beam Θ is fixed at value $= 2^\circ$; scanning range $-15\text{--}80^\circ$; scanning step -0.01° ; scanning speed $-0.2^\circ/\text{min}$; sample rotation speed -30 rpm. The measurements were carried out at room temperature $T = 25^\circ\text{C}$ (298 K). The diffraction patterns were refined using Rietveld refinement via FULLPROF software (Version—July 2017).

Ntegra Spectra atomic force microscope was used to measure the surface topology of the as-grown samples and record Raman spectra (laser $\lambda = 532$ nm). Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer

Lakeshore VSM 7404 (Lake Shore Cryotronics, Inc., Westerville, OH, USA). The chemical composition of the film was determined using energy dispersive X-ray spectroscopy (EDX-spectra, ASPEX Express, Delmont, PA, USA).

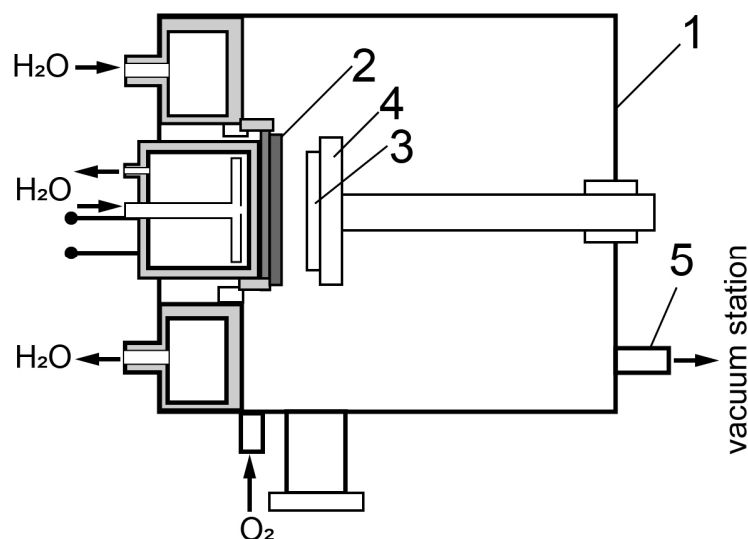


Figure 1. Scheme of the experimental setup for producing heteroepitaxial films. 1—Vacuum chamber, 2—ceramic target, 3—substrate, 4—ceramic heater, 5—output to vacuum station.

For measuring the optical properties we were using an integrating sphere Avasphere-50 (Avantes, Apeldoorn, The Netherlands) in the wavelength range of $\lambda \sim 250\text{--}800\text{ nm}$. The combined deuterium/halogen lamp AvaLight-DH-S-BAL (Avantes, Apeldoorn, The Netherlands) was used as the light source, and its emission was delivered to the samples via a $600\text{ }\mu\text{m}$ fiber optic light guide. Photonic signals were collected using a bifurcated $600\text{ }\mu\text{m}$ light guide and recorded with an MS3504i spectrometer (SOL-Instruments, Minsk, Belarus) combined with an HS-101(HR)-2048 $\times$ 122 CCD camera (Hamamatsu, Hamamatsu City, Japan) and a personal computer. The final data of the spectrophotometric coefficients T_t and R_d were defined as

$$R_d^{exp} = \frac{R_d^s(\lambda) - R_0(\lambda)}{R_{gl}^s(\lambda) - R_0(\lambda)} \text{ and } T_t^{exp} = \frac{T_t^s(\lambda) - T_0(\lambda)}{T_{gl}^s(\lambda) - T_0(\lambda)}, \quad (1)$$

where $T_t^s(\lambda)$ and $R_d^s(\lambda)$ are the transmission and reflection spectra of the samples; $T_{gl}^s(\lambda)$ and $R_{gl}^s(\lambda)$ are the reference signal spectra, measured with quartz plates; $T_0(\lambda)$ is the integrating sphere signal with covered input and open output ports; $R_0(\lambda)$ is the signal for a sphere with open optical ports. The calculation of the spectral dependence of the coefficients of optical absorption μ_a and light scattering μ_s' was carried out using the inverse method of the Monte Carlo numerical simulation, developed and described in detail in the works [20–22].

Overview and region C1s and O1s X-ray photoelectron (XPS) spectra of the samples were collected on SPECS instrument (Specs GmbH, Berlin, Germany) using MgK- α excitation ($E_{ex} = 1254\text{ eV}$). The recorded spectra were calibrated to pure graphite C1s energy (284.6 eV). XPS data were treated with CasaXPS software package (version 2.3.24, Casa Software Ltd., Teignmouth, UK). Shirley type background and mixed Gauss (70%)–Lorentz (30%) functions were used for the deconvolution of spectra under fixed FWHM for all spectral components.

3. Results

The results of the X-ray diffraction studies of a film on a leucosapphire Al₂O₃ (C-plane) substrate annealed at $550\text{ }^\circ\text{C}$ for 2 h are presented in Figure 2. The analysis of the diffraction pattern showed the presence of peaks in good agreement with the standard declared values

for BiFeO_3 (ICSD # 98-015-7424, $R3c$), which can be attributed to rhombohedral planes with space group $R3c$. High intensity peaks related to $\text{Bi}_2\text{Fe}_4\text{O}_9$ (ICSD #98-002-6808, $Pbam$) were also observed.

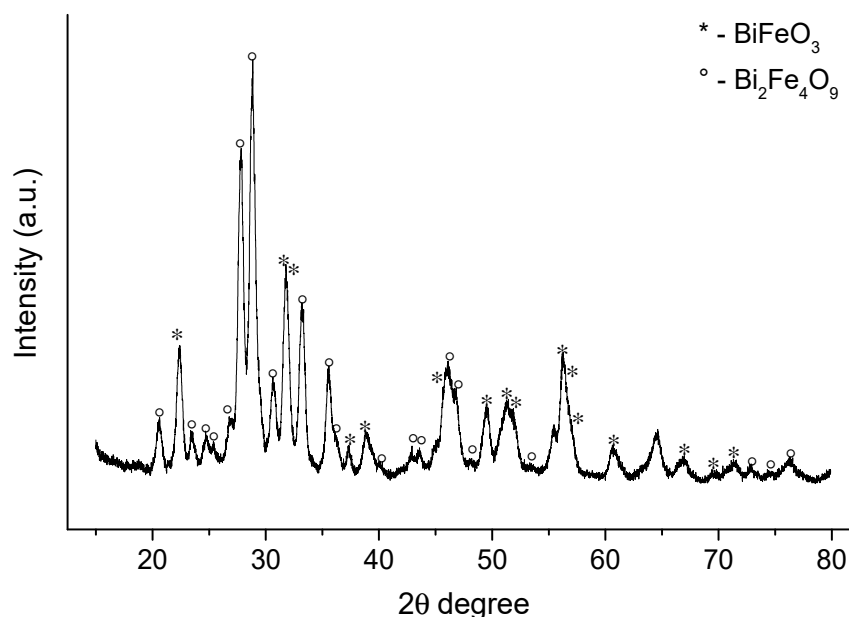


Figure 2. X-ray diffraction pattern of the BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ film.

The volatile nature of bismuth may be responsible for the observed impurity phases. Previously, it was reported that during the synthesis process, the formation of stoichiometric compounds, such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{25}\text{FeO}_{40}$, is inevitable [23–25]. According to previous research, this phenomenon is due to the product transformation during the crystal growth process [26].

The average crystallite size (D) was calculated using the Scherer formula:

$$D = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (2)$$

where K is the shape factor (0.9), λ is the X-ray wavelength, β_{hkl} is the full width at half maximum (FWHM) and θ is the Bragg angle. The calculation was carried out using the peak (012) ($\theta = 22.42^\circ$) for the BiFeO_3 phase and (121) ($\theta = 27.793^\circ$) for the $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase, the average crystallite sizes were 14.9 nm and 17.3 nm, respectively.

The analysis of diffraction patterns using the Rietveld method shows that for the sample under study, the diffraction profile consists of the space group $R3c$, $Pbam$, and $I23$ with the contribution of BiFeO_3 (33.4%), $\text{Bi}_2\text{Fe}_4\text{O}_9$ (63.4%) and a small amount of $\text{Bi}_{25}\text{FeO}_{40}$ (3.2%) (Figure 3, Table 1). The content of $\text{Bi}_{25}\text{FeO}_{40}$ (ICSD #98-004-1937, $I23$) is quite small and within acceptable limits, and the contribution of its influence on the properties of the BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ composite can be excluded. The refined lattice parameters and crystallite size are presented in Table 1.

Table 1. Structural parameters and average crystallite size.

Phase	Lattice Parameters			Crystallite Size (nm)	Phase Fraction (%)	R-Factors and χ^2
	a	b	c			
BiFeO_3	5.6010	5.6010	13.8125	14.9	33.4%	R profile—14.05 R expected—6.68 χ^2 —7.2
$\text{Bi}_2\text{Fe}_4\text{O}_9$	7.8954	8.5891	6.0582	17.3	63.4%	
$\text{Bi}_{25}\text{FeO}_{40}$	9.8677	9.8677	9.8677	16.5	3.2%	

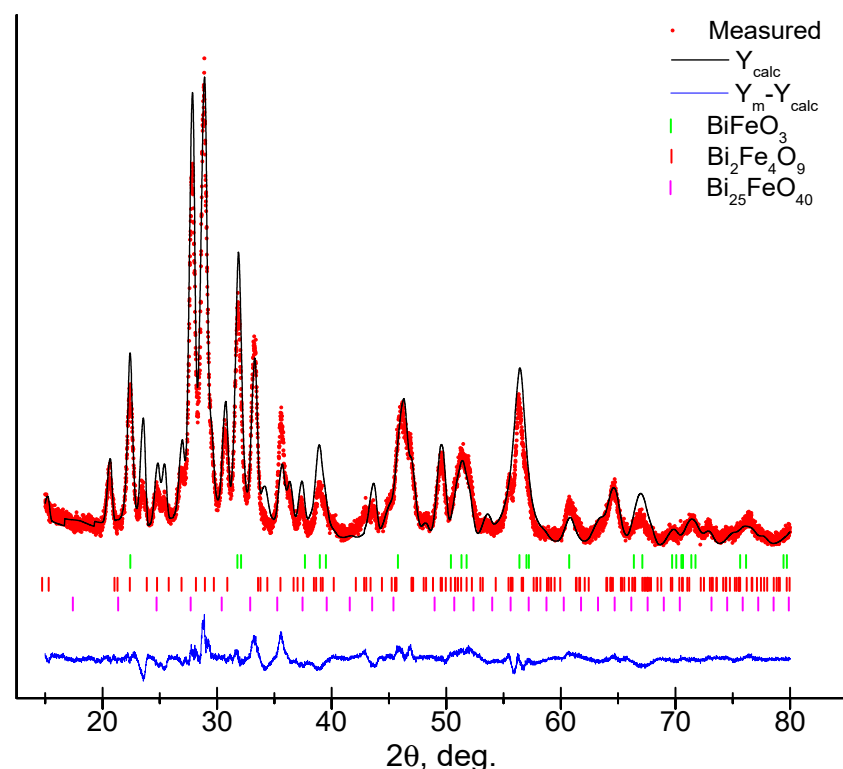


Figure 3. Refined X-ray diffraction pattern of a thin film using the Rietveld method.

Raman scattering is one of the most powerful tools used to study structural features. Figure 4 shows the Raman spectrum in the range $100\text{--}1000\text{ cm}^{-1}$, showing the characteristic peaks expected for the BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases.

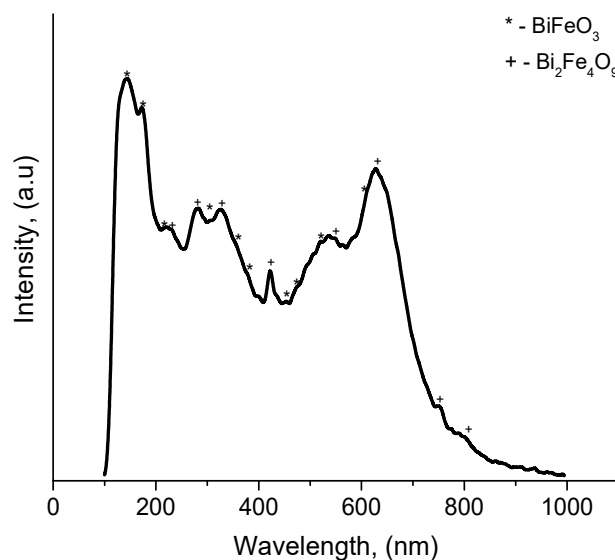


Figure 4. Raman spectra of $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$ film.

Note that for the compounds BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$, despite being well-studied by Raman spectroscopy methods, there are discrepancies in the results in the literature. According to group theory [27,28], a rhombohedral BFO with space group $R3c$ is characterized by thirteen ($4A_1 + 9E$) active modes. Also, in [29], they showed that the mullite compound $\text{Bi}_2\text{Fe}_4\text{O}_9$ is characterized by the presence of forty-two combination modes in the phonon spectrum out of a total number of ninety zone-center (Γ -point) modes in the Ra-

man spectrum. However, as in the case of BiFeO_3 , for $\text{Bi}_2\text{Fe}_4\text{O}_9$, in practice, a smaller number of phonon modes is observed compared to the above group-theoretic representation [28,30]. Table 2 shows the experimentally observed values of the Raman modes. The spectrum shows two distinct peaks at 143 and 175 cm^{-1} and eight weaker peaks in the range 218 – 609 cm^{-1} . In the case of $\text{Bi}_2\text{Fe}_4\text{O}_9$, clearly defined modes can be distinguished at 280 , 328 , and 423 cm^{-1} . The observed Raman modes are in good agreement with the Raman spectra of BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ single crystals [29,31,32].

Table 2. Raman mode values (in cm^{-1}).

BiFeO_3	143	175	218	305	358	380	455	473	517	609
$\text{Bi}_2\text{Fe}_4\text{O}_9$	232	280	328	423	546	630	752	807	-	-

Thus, the results of the Raman analysis are in good agreement with the results of the X-ray diffraction analysis, confirming the coexistence of both rhombohedral BiFeO_3 and orthorhombic $\text{Bi}_2\text{Fe}_4\text{O}_9$.

The surface topography of a BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ composite thin film with a scale area of $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ obtained by AFM is shown in Figure 5. The BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ film has a dense surface without voids and cracks. The dense surface morphology and the absence of cracks and voids confirm the uniform deposition of thin films, suitable for the subsequent design of devices based on them. The analysis of the AFM image of the film shows that the grains on the surface are large compared to the size of their crystallites calculated using the Scherrer formula. In general, the grain size was in the range of 20 – 80 nm , and the average size was about 48 nm . The widely varying values of the crystallite size and grain size indicate that the latter are not single crystalline, but rather consist of many crystallites. The root mean square roughness (Rms) of the BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ thin film was 11.14 nm .

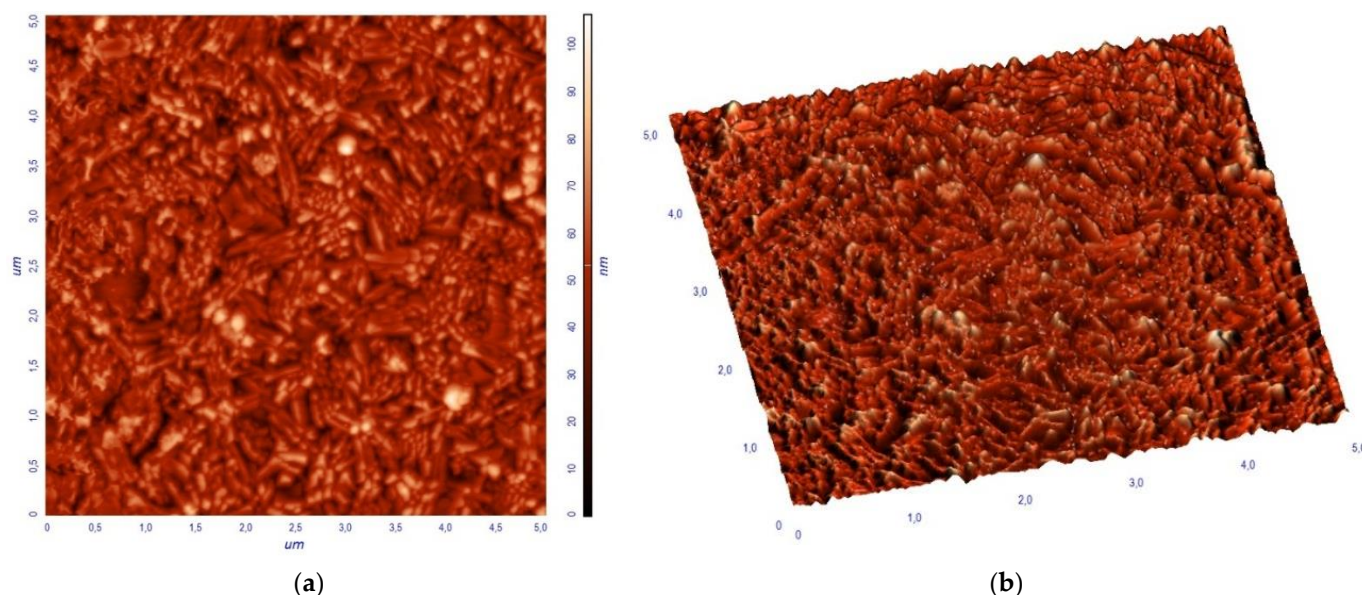


Figure 5. AFM images of the BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ thin films: (a) 2D, (b) 3D.

The results of studying the full energy spectrum of the BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ composite film using energy dispersive X-ray spectroscopy (EDX) are presented in Figure 6. The elemental composition of the sample corresponds to the chemical formulas of the components and corresponds to the results of X-ray diffraction analysis. The EDX spectra were taken in several selected areas of the sample, and all showed the expected presence of Bi, Fe, and O. An Al peak associated with the Al_2O_3 substrate is also observed. The presence of a carbon peak is related to the research methodology.

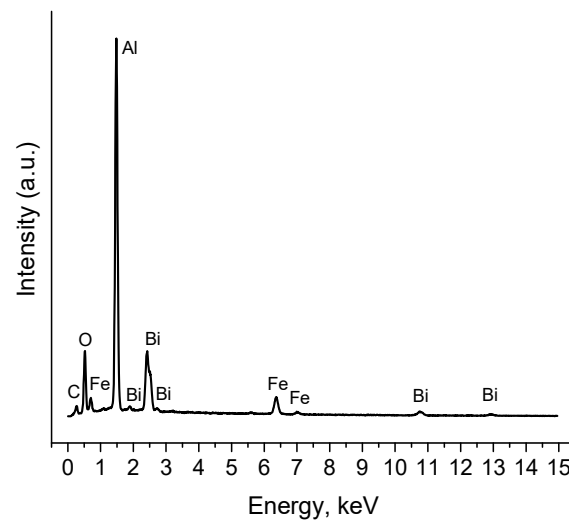


Figure 6. EDX spectrum of the BiFeO₃-Bi₂Fe₄O₉ film.

The optical properties of the BiFeO₃-Bi₂Fe₄O₉ nanocomposite were studied using UV-visible diffuse reflectance spectroscopy and converted into absorption spectra using the Monte Carlo method [20,22]. The absorption spectrum in the wavelength range 250–800 nm is shown in Figure 7.

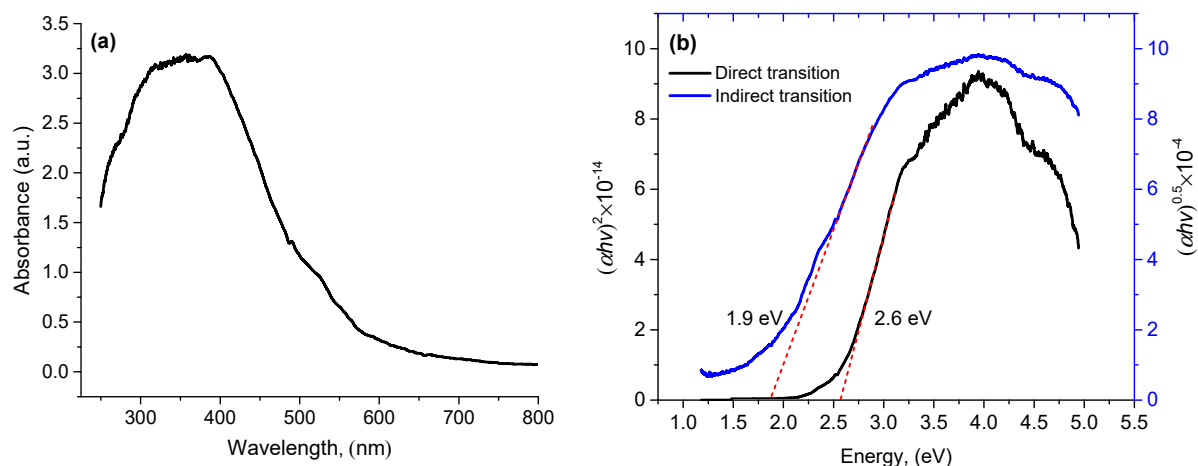


Figure 7. UV-visible spectra of a thin film (a) and Tauc plot of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{0.5}$ versus $h\nu$ for the optical band gap E_g (b).

As can be seen, the sample exhibits absorption in the ultraviolet and visible regions of light. The optical band gap (E_g) can be estimated using the Tauc relation [33,34]:

$$(\alpha h\nu) = K(h\nu - E_g)^n \quad (3)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, K is a constant, n is the coefficient characterizing the direct or indirect optical transition. The value of the band gap is determined by interpolating the linear part of the graph to the X axis. The linear regions on the Tauc plots (Figure 7b) indicate either an indirect optical band gap of 1.9 eV or a direct optical band gap of 2.6 eV. The existing literature indicates a wide band gap range (2.1–2.8 eV) for BiFeO₃ and indicates the existence of both direct and indirect electron photoexcitation at room temperature in BiFeO₃. However, the indirect charge transfer mechanism is thought to predominate at low room temperatures [35]. In the case of Bi₂Fe₄O₉ films, the optical band gap is in the range of 2.05–2.2 eV [36–38]. From the theoretical studies of density functional theory [37], the band gap of Bi₂Fe₄O₉ is considered

to be indirect. For the $\text{Bi}_2\text{Fe}_4\text{O}_9$ - BiFeO_3 sample, a band gap of 2.1 eV was observed [39]. Based on an analysis of the literature and the fact that the $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase predominates in our sample, we believe that in our case, an indirect optical transition occurs.

Figure 8a shows the results of a panoramic scan of a thin film. Only C 1s, O 1s, Bi 4f and Fe 2p peaks were detected, indicating the absence of impurities, which is also confirmed by the EDX spectrum. The C 1s peak is due to carbon impurities [40,41]. Three regions associated with the Bi 4f, Fe 2p, and O 1s in the panoramic XPS spectrum of the sample were studied.

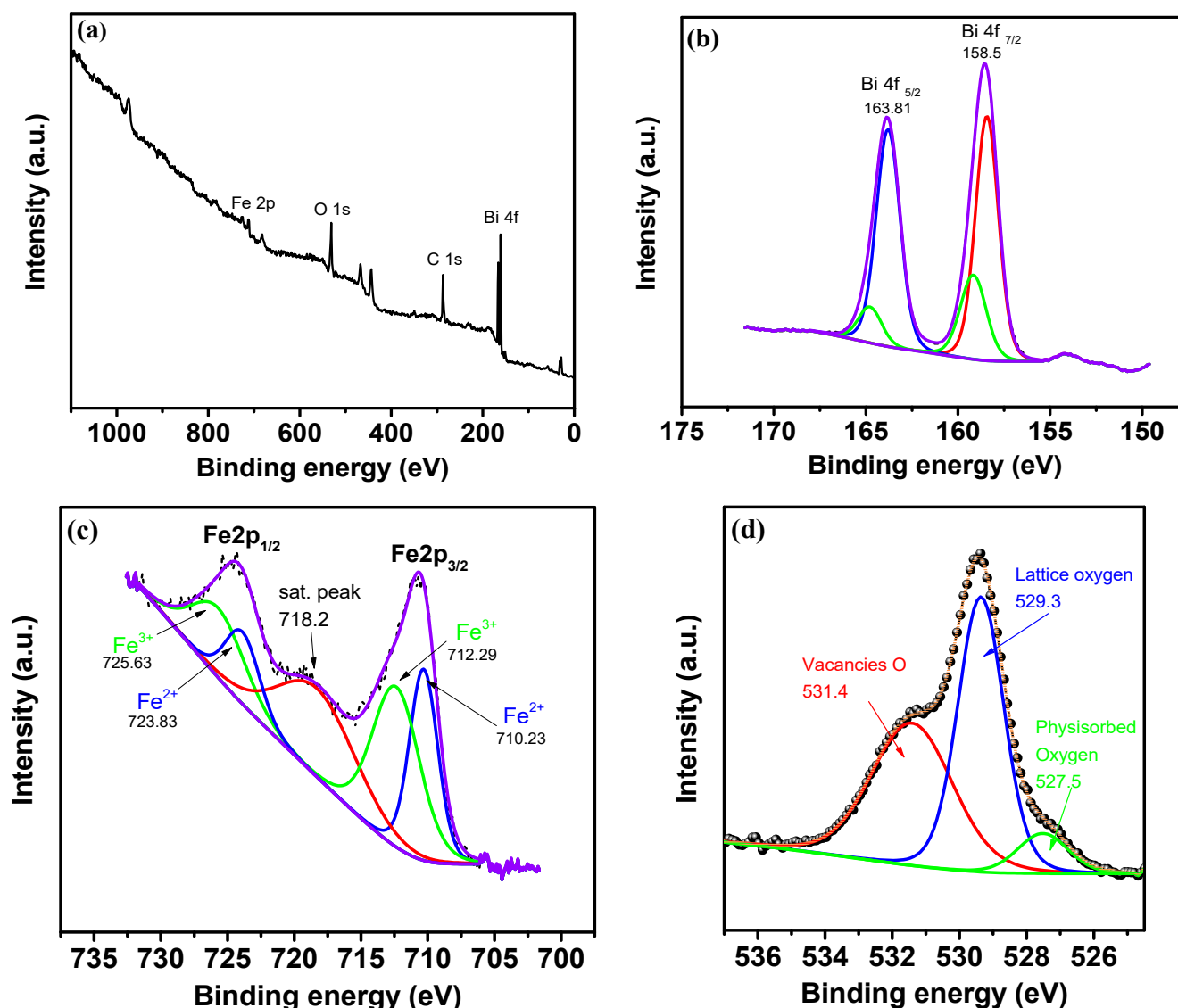


Figure 8. XPS spectra of BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ composite film: panoramic spectra (a); Bi 4f (b); Fe 2p (c); O 1s (d).

The high resolution Bi 4f spectra for the BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ composite are shown in Figure 8b. The Bi 4f doublet consists of two peaks at 163.81 and 158.5 eV, which confirm the 3^+ oxidation state of Bi, mainly representing the Bi-O bond. The spin-orbit splitting energy was $\Delta = 5.31$ eV, which is comparable to the literature data [41–43] and is in good agreement with the theoretical value of 5.31 eV [44]. Two selected sub-peaks located at 163.74 and 158.31 eV are attributed to Bi ($4f_{5/2}$)-O and Bi ($4f_{7/2}$)-O bonds, while the other sub-peaks, located at 164.75 and 159.11 eV, can be attributed to the Bi-O-Fe bond in the FeO_6 octahedron, caused by oxygen vacancies and cation defects [45,46].

The spectra of the main level of Fe 2p are shown in Figure 8c. The asymmetric nature of the peaks and the presence of satellite peaks indicate the presence of iron in the oxidation states of Fe²⁺ and Fe³⁺. As shown in Figure 8c, the curve is divided into five components. The peaks of the Fe 2p doublets are concentrated at 724.31 eV (Fe³⁺ 2p_{1/2}) and 710.63 eV (Fe³⁺ 2p_{3/2}), which represent Fe–O bonds [45]. The spin-orbit splitting energy of pure Fe 2p is 13.68 eV, which is close to the theoretical value (Δ Fe 2p) of 13.6 eV for Fe₂O₃ [45]. The peaks of the Fe 2p doublets located at 725.63 eV and 712.29 eV can be attributed to the (Fe 2p_{1/2})₂–O₃ and (Fe 2p_{3/2})–O₃ bonds, and the subpeaks located at 723.83 and 710.23 to the bonds Fe–O, Fe–O–Bi bonds in the FeO₆ octahedron, oxygen vacancies, and cation defects [47].

According to the ratio of the fitted peak areas for Fe³⁺ and Fe²⁺, the concentration ratio of Fe³⁺ and Fe²⁺ is approximately 1.43, indicating a relatively high Fe²⁺ content, which in turn may affect the magnetic properties of the composite.

To confirm the presence of oxygen vacancies, the spectrum of the O 1s level was studied. Figure 8d shows the O 1s spectra after deconvolution with the approximation of the fitted peaks. The spectrum is well-described by the superposition of three components centered at 527.5, 529.3, and 531.4 eV, respectively. A strong peak at 529.3 eV is assigned to the characteristic signal from lattice O. The shoulder at about 531.4 eV belongs to defective O components, such as oxygen vacancies, and the peak at 527.5 to physisorbed oxygen [42].

Figure 9a shows the magnetic hysteresis loops M–H of the BiFeO₃–Bi₂Fe₄O₉ composite structure, measured at room temperature in magnetic fields up to 20 kOe. Figure 9b shows the M–H loop considering the subtraction of the diamagnetic contribution of the substrate. The loop exhibits a ferromagnetic character without reaching saturation. The presence of magnetic hysteresis indicates the ferromagnetic properties of the resulting films, while the substrate exhibits diamagnetic properties.

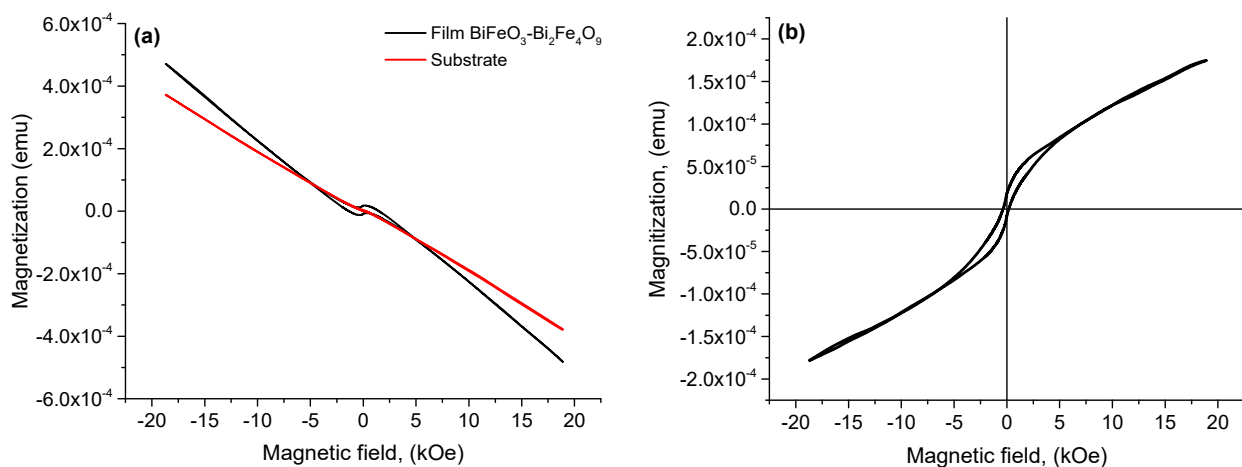


Figure 9. M–H magnetic hysteresis loops before (a) and after (b) subtraction of the diamagnetic contribution of the substrate.

Since in the maximum magnetic fields achieved by a laboratory vibration magnetometer the magnetization did not reach saturation, the law of approach to saturation (LAS) was applied to estimate the value of saturation magnetization M_s . The LAS determines the dependence of magnetization (M) on the applied field (H), where the applied field (H) is much greater than the coercive field (H_C). LAS is usually used to describe magnetization in a region of strong magnetic field, where the rotation of the magnetic domain plays a significant role. According to [48] this value is determined by the expression:

$$M = M_s \left[1 - \frac{a}{H} - \frac{b}{H^2} \right] + kH \quad (4)$$

A typical LAS fitting curve for the $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$ is shown in Figure 10. For this sample, the saturation magnetization, remanence, and coercive force were $M_s = 1.59 \times 10^{-4}$ emu, $M_r = 1.33 \times 10^{-5}$ emu and $H_C = 270$ Oe, respectively and the $M_r/M_s = 0.0833$.

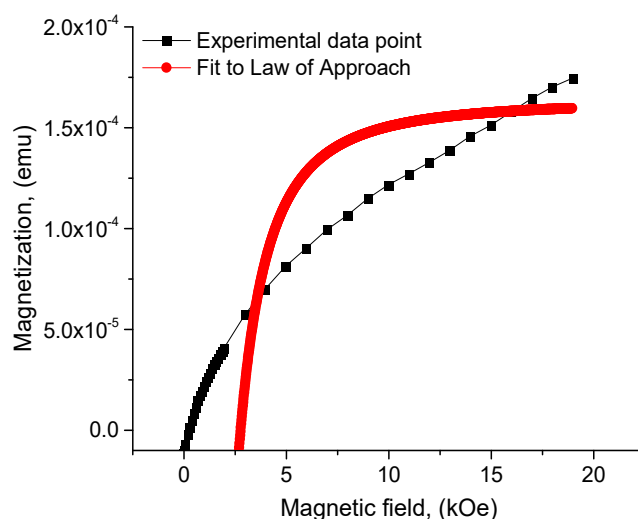


Figure 10. Fitting to the law of approach to saturation (LAS) for $\text{Bi}_2\text{Fe}_4\text{O}_9\text{-BiFeO}_3$.

Note that a wasp-waist hysteresis loop was observed in the sample. Work by Lawrence H. Bennett and Edward Della Torre [49] examined how wasp-waist hysteresis loops arise in composite materials containing two ferromagnetic materials with different coercivities. Roberts and his colleagues, as well as Tauxe and his colleagues, used numerical simulations to determine the causes of this phenomenon. They found that the coexistence of materials with different properties, such as magnetic hardness and softness, anisotropy and coercive fields, or a mixture of single-domain and superparamagnetic particles can explain the appearance of the wasp-waist hysteresis loop [50–52].

4. Conclusions

By using the radio frequency cathode sputtering method of a ceramic target with a stoichiometric composition of BiFeO_3 in an oxygen atmosphere, the nanocomposite films $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$ were obtained on a sapphire substrate Al_2O_3 . Based on the results of the film analysis using X-ray structural analysis, Raman scattering, XPS, and atomic force microscopy, the structural parameters, topography, chemical composition of the films, concentration, and average sizes of the crystallites for each phase were determined. The results of the structural analysis demonstrated the formation of a two-phase structure, consisting of BiFeO_3 (33.4%), $\text{Bi}_2\text{Fe}_4\text{O}_9$ (63.4%), and a small amount of $\text{Bi}_{25}\text{FeO}_{40}$ (3.2%). The grain sizes, determined by AFM, were approximately 48 nm, and the root mean square roughness (Rms) of the film was 11 nm. The bandgap width was 1.9 eV for an indirect and 2.6 eV for a direct interband transition. The magnetic properties were characterized by a hysteresis loop resembling a wasp-waist, indicating the presence of magnetic anisotropy. The saturation magnetization, remanence, and coercive force were $M_s = 1.59 \times 10^{-4}$ emu, $M_r = 1.33 \times 10^{-5}$ emu, and $H_C = 270$ Oe, respectively, with a M_r/M_s ratio of 0.0833. The results of the research can be useful in creating new materials for magnetoelectronics.

Author Contributions: Conceptualization, F.O. and N.A.; methodology, S.K. and N.A.; validation, S.S., J.M. and K.G.; formal analysis, S.S., M.A. and K.G.; investigation, A.P., M.A., J.M. and N.A.; resources, A.P. and F.O.; data curation, S.K.; writing—original draft preparation, S.K. and N.A.; writing—review and editing, S.S., A.P. and F.O.; visualization, M.A.; supervision, S.K., F.O. and K.G.; project administration, F.O.; funding acquisition, J.M. All authors have read and agreed to the published version of the manuscript.

Funding: The work was carried out with the financial support of the Russian Science Foundation grant, project number 23-22-00130.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data can be provided upon request to the corresponding author.

Acknowledgments: The CzechNanoLab project LM2023051 funded by MEYS CR is gratefully acknowledged for the financial support of the measurements at CEITEC Nano Research Infrastructure. The authors also acknowledge the shared services center “Surface and novel materials” of UdmFRC of UB RAS for the XPS data acquisition using the SPECS spectrometer. The X-ray diffraction studies were performed on the equipment of the Analytical Center for Collective Use of the Dagestan Federal Research Center of the Russian Academy of Sciences.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Catalan, G.; Scott, J.F. Physics and Applications of Bismuth Ferrite. *Adv. Mater.* **2009**, *21*, 2463–2485. [\[CrossRef\]](#)
2. Ramazanov, S.; Sobola, D.; Gajiev, G.; Orudzhiev, F.; Kaspar, P.; Gummetov, A. Multiferroic/Polymer Flexible Structures Obtained by Atomic Layer Deposition. *Nanomaterials* **2022**, *13*, 139. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Sando, D.; Agbelele, A.; Rahmedov, D.; Liu, J.; Rovillain, P.; Toulouse, C.; Infante, I.C.; Pyatakov, A.P.; Fusil, S.; Jacquet, E.; et al. Crafting the Magnonic and Spintronic Response of BiFeO₃ Films by Epitaxial Strain. *Nat. Mater.* **2013**, *12*, 641–646. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Lee, J.H.; Fina, I.; Marti, X.; Kim, Y.H.; Hesse, D.; Alexe, M.; Lee, J.H.; Fina, I.; Kim, Y.H.; Hesse, D.; et al. Spintronic Functionality of BiFeO₃ Domain Walls. *Adv. Mater.* **2014**, *26*, 7078–7082. [\[CrossRef\]](#)
5. Smolenskii, G.A.; Yudin, V.M.; Sher, E. Weak ferromagnetism of some BiFeO₃-Pb(Fe_{0.5}Nb_{0.5})O₃ perovskites. *Sov. Phys. Solid State* **1965**, *6*, 2936.
6. Sosnowska, I.; Peterlin-Neumaier, T.; Steichele, E. Spiral Magnetic Ordering in Bismuth Ferrite. *J. Phys. C Solid State Phys.* **1982**, *15*, 4835–4846. [\[CrossRef\]](#)
7. Maity, T.; Goswami, S.; Bhattacharya, D.; Roy, S. Superspin Glass Mediated Giant Spontaneous Exchange Bias in a Nanocomposite of BiFeO₃-Bi₂Fe₄O₉. *Phys. Rev. Lett.* **2013**, *110*, 107201. [\[CrossRef\]](#)
8. Maity, T.; Roy, S. Asymmetric Ascending and Descending Loop Shift Exchange Bias in Bi₂Fe₄O₉-BiFeO₃ Nanocomposites. *J. Magn. Magn. Mater.* **2020**, *494*, 165783. [\[CrossRef\]](#)
9. Pleshakov, I.V.; Volkov, M.P.; Lomanova, N.A.; Kuz'min, Y.I.; Gusarov, V.V. Magnetic Characteristics of a Nanocomposite Based on Bismuth Ferrites. *Tech. Phys. Lett.* **2020**, *46*, 1072–1075. [\[CrossRef\]](#)
10. Park, Y.A.; Song, K.M.; Lee, K.D.; Won, C.J.; Hur, N. Effect of Antiferromagnetic Order on the Dielectric Properties of Bi₂Fe₄O₉. *Appl. Phys. Lett.* **2010**, *96*, 338992. [\[CrossRef\]](#)
11. Dutta, D.P.; Sudakar, C.; Mocherla, P.S.V.; Mandal, B.P.; Jayakumar, O.D.; Tyagi, A.K. Enhanced Magnetic and Ferroelectric Properties in Scandium Doped Nano Bi₂Fe₄O₉. *Mater. Chem. Phys.* **2012**, *135*, 998–1004. [\[CrossRef\]](#)
12. Kirsch, A.; Murshed, M.M.; Litterst, F.J.; Gesing, T.M. Structural, Spectroscopic, and Thermoanalytic Studies on Bi₂Fe₄O₉: Tunable Properties Driven by Nano- and Poly-Crystalline States. *J. Phys. Chem. C* **2019**, *123*, 3161–3171. [\[CrossRef\]](#)
13. Zhao, J.; Liu, T.; Xu, Y.; He, Y.; Chen, W. Synthesis and Characterization of Bi₂Fe₄O₉ Powders. *Mater. Chem. Phys.* **2011**, *128*, 388–391. [\[CrossRef\]](#)
14. Alvarez, G.; Contreras, J.; Conde-Gallardo, A.; Montiel, H.; Zamorano, R. Detection of Para–Antiferromagnetic Transition in Bi₂Fe₄O₉ Powders by Means of Microwave Absorption Measurements. *J. Magn. Magn. Mater.* **2013**, *348*, 17–21. [\[CrossRef\]](#)
15. Papaefthymiou, G.C.; Viescas, A.J.; Le Breton, J.M.; Chiron, H.; Juraszek, J.; Park, T.J.; Wong, S.S. Magnetic and Mössbauer Characterization of the Magnetic Properties of Single-Crystalline Sub-Micron Sized Bi₂Fe₄O₉ Cubes. *Curr. Appl. Phys.* **2015**, *15*, 417–422. [\[CrossRef\]](#)
16. Tian, Z.M.; Yuan, S.L.; Wang, X.L.; Zheng, X.F.; Yin, S.Y.; Wang, C.H.; Liu, L. Size Effect on Magnetic and Ferroelectric Properties in Bi₂Fe₄O₉ Multiferroic Ceramics. *J. Appl. Phys.* **2009**, *106*, 343219. [\[CrossRef\]](#)
17. Zvezdin, A.K.; Pyatakov, A.P. Phase transitions and the giant magnetoelectric effect in multiferroics. *Phys.-Uspekhi* **2004**, *47*, 416. [\[CrossRef\]](#)
18. Yuan, G.L.; Or, S.W.; Chan, H.L.W.; Liu, Z.G. Reduced Ferroelectric Coercivity in Multiferroic Bi_{0.825}Nd_{0.175}FeO₃ Thin Film. *J. Appl. Phys.* **2007**, *101*, 818138. [\[CrossRef\]](#)
19. Zhang, T.; Shen, Y.; Qiu, Y.; Liu, Y.; Xiong, R.; Shi, J.; Wei, J. Facial Synthesis and Photoreaction Mechanism of BiFeO₃/Bi₂Fe₄O₉ Heterojunction Nanofibers. *ACS Sustain. Chem. Eng.* **2017**, *5*, 4630–4636. [\[CrossRef\]](#)
20. Wang, L.; Steven, L.; Jacques, P.D. *Monte Carlo Modeling of Light Transport in Multi-Layered Tissues in Standard C*; University of Texas M. D. Anderson Cancer Center: Houston, TX, USA, 1992.

21. Giraev, K.M.; Ashurbekov, N.A.; Magomedov, M.A.; Murtazaeva, A.A.; Medzhidov, R.T. The Effect of Pathological Processes on Absorption and Scattering Spectra of Samples of Bile and Pancreatic Juice. *Opt. Spectrosc. Engl. Transl. Opt. I Spektrosk.* **2015**, *119*, 162–170. [\[CrossRef\]](#)
22. Orudzhev, F.; Alikhanov, N.; Amirov, A.; Rabadanova, A.; Selimov, D.; Shuaibov, A.; Gulakhmedov, R.; Abdurakhmanov, M.; Magomedova, A.; Ramazanov, S.; et al. Porous Hybrid PVDF/BiFeO₃ Smart Composite with Magnetic, Piezophotocatalytic, and Light-Emission Properties. *Catalysts* **2023**, *13*, 874. [\[CrossRef\]](#)
23. Huo, Y.; Jin, Y.; Zhang, Y. Citric Acid Assisted Solvothermal Synthesis of BiFeO₃ Microspheres with High Visible-Light Photocatalytic Activity. *J. Mol. Catal. A Chem.* **2010**, *331*, 15–20. [\[CrossRef\]](#)
24. Selbach, S.M.; Tybell, T.; Einarsrud, M.A.; Grande, T. Size-Dependent Properties of Multiferroic BiFeO₃ Nanoparticles. *Chem. Mater.* **2007**, *19*, 6478–6484. [\[CrossRef\]](#)
25. Li, S.; Lin, Y.H.; Zhang, B.P.; Wang, Y.; Nan, C.W. Controlled Fabrication of BiFeO₃ Uniform Microcrystals and Their Magnetic and Photocatalytic Behaviors. *J. Phys. Chem. C* **2010**, *114*, 2903–2908. [\[CrossRef\]](#)
26. Dai, Z.; Akishige, Y. Electrical Properties of Multiferroic BiFeO₃ Ceramics Synthesized by Spark Plasma Sintering. *J. Phys. D Appl. Phys.* **2010**, *43*, 445403. [\[CrossRef\]](#)
27. Fukumura, H.; Harima, H.; Kisoda, K.; Tamada, M.; Noguchi, Y.; Miyayama, M. Raman Scattering Study of Multiferroic BiFeO₃ Single Crystal. *J. Magn. Magn. Mater.* **2007**, *310*, e367–e369. [\[CrossRef\]](#)
28. Bielecki, J.; Svedlindh, P.; Tibebu, D.T.; Cai, S.; Eriksson, S.G.; Börjesson, L.; Knee, C.S. Structural and Magnetic Properties of Isovalently Substituted Multiferroic BiFeO₃: Insights from Raman Spectroscopy. *Phys. Rev. B Condens. Matter. Mater. Phys.* **2012**, *86*, 184422. [\[CrossRef\]](#)
29. Iliev, M.N.; Litvinchuk, A.P.; Hadjiev, V.G.; Gospodinov, M.M.; Skumryev, V.; Ressouche, E. Phonon and Magnon Scattering of Antiferromagnetic Bi₂Fe₄O₉. *Phys. Rev. B Condens. Matter. Mater. Phys.* **2010**, *81*, 024302. [\[CrossRef\]](#)
30. Mohapatra, S.R.; Swain, A.; Yadav, C.S.; Kaushik, S.D.; Singh, A.K. Unequivocal Evidence of Enhanced Magnetodielectric Coupling in Gd³⁺ Substituted Multiferroic Bi₂Fe₄O₉. *RSC Adv.* **2016**, *6*, 112282–112291. [\[CrossRef\]](#)
31. Alikhanov, N.M.R.; Rabadanov, M.K.; Orudzhev, F.F.; Gadzhimagomedov, S.K.; Emirov, R.M.; Sadykov, S.A.; Kallaev, S.N.; Ramazanov, S.M.; Abdulvakhidov, K.G.; Sobola, D. Size-Dependent Structural Parameters, Optical, and Magnetic Properties of Facile Synthesized Pure-Phase BiFeO₃. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 13323–13335. [\[CrossRef\]](#)
32. Friedrich, A.; Biehler, J.; Morgenroth, W.; Wiehl, L.; Winkler, B.; Hanfland, M.; Tolkiehn, M.; Burianek, M.; Mühlberg, M. High-Pressure Phase Transition of Bi₂Fe₄O₉. *J. Phys. Condens. Matter* **2012**, *24*, 145401. [\[CrossRef\]](#)
33. Zeljković, S.; Ivas, T.; Maruyama, H.; Nino, J.C. Structural, Magnetic and Optical Properties of BiFeO₃ Synthesized by the Solvent-Deficient Method. *Ceram. Int.* **2019**, *45*, 19793–19798. [\[CrossRef\]](#)
34. Tu, C.S.; Chen, P.Y.; Jou, Y.S.; Chen, C.S.; Chien, R.R.; Schmidt, V.H.; Haw, S.C. Polarization-Modulated Photovoltaic Conversion in Polycrystalline Bismuth Ferrite. *Acta Mater.* **2019**, *176*, 1–10. [\[CrossRef\]](#)
35. Wang, Y.; Daboczi, M.; Zhang, M.; Briscoe, J.; Kim, J.S.; Yan, H.; Dunn, S. Origin of the switchable photocurrent direction in BiFeO₃ thin films. *Mater. Horiz.* **2023**. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Zeng, T.; Liu, Z.; Huang, G.; Hou, J.; Zhang, G. Visible-light photovoltaic effect in multiferroic Bi₂Fe₄O₉ thin film. *Mater. Lett.* **2022**, *309*, 131411. [\[CrossRef\]](#)
37. Ameer, S.; Jindal, K.; Tomar, M.; Jha, P.K.; Gupta, V. Growth of highly oriented orthorhombic phase of Bi₂Fe₄O₉ thin films by pulsed laser deposition. *Mater. Today Proc.* **2021**, *47*, 1646–1650. [\[CrossRef\]](#)
38. Liu, Y.; Zuo, R. Morphology and optical absorption of Bi₂Fe₄O₉ crystals via mineralizer-assisted hydrothermal synthesis. *Particuology* **2013**, *11*, 581–587. [\[CrossRef\]](#)
39. Psathas, P.; Georgiou, Y.; Moularas, C.; Armatas, G.S.; Deligiannakis, Y. Controlled-Phase Synthesis of Bi₂Fe₄O₉ & BiFeO₃ by Flame Spray Pyrolysis and their evaluation as non-noble metal catalysts for efficient reduction of 4-nitrophenol. *Powder Technol.* **2020**, *368*, 268–277. [\[CrossRef\]](#)
40. Zhong, Y.; Ma, Y.; Guo, Q.; Liu, J.; Wang, Y.; Yang, M.; Xia, H. Controllable synthesis of TiO₂@Fe₂O₃ core-shell nanotube arrays with double-wall coating as superb lithium-ion battery anodes. *Sci. Rep.* **2017**, *7*, 40927. [\[CrossRef\]](#)
41. Gomez-Iriarte, G.A.; Pentón-Madrigal, A.; de Oliveira, L.A.S.; Sinnecker, J.P. XPS study in BiFeO₃ surface modified by argon etching. *Materials* **2022**, *15*, 4285. [\[CrossRef\]](#)
42. Zhang, C.; Wang, S.Y.; Liu, W.F.; Xu, X.L.; Li, X.; Zhang, H.; Gao, J.; Li, D.J. Room temperature exchange bias in multiferroic BiFeO₃ nano- and microcrystals with antiferromagnetic core and two-dimensional diluted antiferromagnetic shell. *J. Nanopart. Res.* **2017**, *19*, 182. [\[CrossRef\]](#)
43. Bharathkumar, S.; Sakar, M.; Balakumar, S. Versatility of electrospinning in the fabrication of fibrous mat and mesh nanostructures of bismuth ferrite (BiFeO₃) and their magnetic and photocatalytic activities. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17745–17754. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Xue, X.; Tan, G.; Liu, W.; Ren, H. Structural, electrical and magnetic properties of (Bi_{0.9}RE_{0.1})(Fe_{0.97}Co_{0.03})O₃ (RE = Nd and Gd) thin films. *Mater. Res. Bull.* **2014**, *52*, 143–150. [\[CrossRef\]](#)
45. Quan, Z.; Hu, H.; Xu, S.; Liu, W.; Fang, G.; Li, M.; Zhao, X. Surface chemical bonding states and ferroelectricity of Ce-doped BiFeO₃ thin films prepared by sol-gel process. *J. Sol-Gel Sci. Technol.* **2008**, *48*, 261–266. [\[CrossRef\]](#)
46. Wang, J.B.N.J.; Neaton, J.B.; Zheng, H.; Nagarajan, V.; Ogale, S.B.; Liu, B.; Viehland, D.; Vaithyanathan, V.; Schlom, D.G.; Waghmare, U.V.; et al. Epitaxial BiFeO₃ multiferroic thin film heterostructures. *Science* **2003**, *299*, 1719–1722. [\[CrossRef\]](#)

47. Tamilselvan, A.; Balakumar, S.; Sakar, M.; Nayek, C.; Murugavel, P.; Kumar, K.S. Role of oxygen vacancy and Fe–O–Fe bond angle in compositional, magnetic, and dielectric relaxation on Eu-substituted BiFeO₃ nanoparticles. *Dalton Trans.* **2014**, *43*, 5731–5738. [[CrossRef](#)] [[PubMed](#)]
48. Paswan, S.K.; Kumari, S.; Kar, M.; Singh, A.; Pathak, H.; Borah, J.P.; Kumar, L. Optimization of Structure-Property Relationships in Nickel Ferrite Nanoparticles Annealed at Different Temperature. *J. Phys. Chem. Solids* **2021**, *151*, 109928. [[CrossRef](#)]
49. Bennett, L.H.; Della Torre, E. Analysis of Wasp-Waist Hysteresis Loops. *J. Appl. Phys.* **2005**, *97*, 984370. [[CrossRef](#)]
50. Gupta, S.; Tomar, M.; Gupta, V. Magnetic Hysteresis of Cerium Doped Bismuth Ferrite Thin Films. *J. Magn. Magn. Mater.* **2015**, *378*, 333–339. [[CrossRef](#)]
51. Roberts, A.P.; Cui, Y.; Verosub, K.L. Wasp-Waisted Hysteresis Loops: Mineral Magnetic Characteristics and Discrimination of Components in Mixed Magnetic Systems. *J. Geophys. Res. Solid Earth* **1995**, *100*, 17909–17924. [[CrossRef](#)]
52. Tauxe, L.; Mullender, T.A.T.; Pick, T. Potbellies, Wasp-Waists, and Superparamagnetism in Magnetic Hysteresis. *J. Geophys. Res. Solid Earth* **1996**, *101*, 571–583. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.